MINERAL-SURFACTANT INTERACTIONS FOR MINIMUM REAGENTS PRECIPITATION AND ADSORPTION FOR IMPROVED OIL RECOVERY

TECHNICAL PROGRESS REPORT

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Principle Author: Prof. P. Somasundaran

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Principal Investigator Prof. P. Somasundaran

Submitting Organization
Office of Projects and Grants
Columbia University in the City of New York
1210 Amsterdam Avenue, Mail Code 2205
Room 254 Engineering Terrace
New York, NY 10027

Contracting Officer's Representative
Sue Mehlhoff
U.S. Department of Energy,
National Petroleum Technology Office
One West Third Street, Suit 1400
Tulsa, Oklahoma 74101-3519

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ABSTRACT

In this project, fundamental studies were conducted to understand the mechanisms of the interactions between polymers/surfactants and minerals with the aim of minimizing chemical loss by adsorption. The effects of structures of the surface active molecules on critical solid/liquid interfacial properties such as adsorption, wettability and surface tension in mineral/surfactant systems were investigated. The final aim is to build a guideline to design optimal polymer/surfactant formula based on the understanding of adsorption and orientation of surfactants and their aggregates at solid/liquid interfaces.

During this period, the wettability of alumina was tested using two-phase extraction at different pHs. The results were explained using the adsorption data obtain previously. It was found that the wettability is determined by both the nano-structure of the hemimicelles and the surface coverage. It was found that pH plays a critical role in controlling the total adsorption and the mineral wattability. At pH 4, the alumina surface remains hydrophilic in the surfactant concentration range tested because of the low surface coverage, even though hemimicelles are formed.

Adsorption of sodium dodecyl sulfate (SDS) on alumina and silica, the component minerals reservoir rocks, was conducted at different pHs. The adsorption of SDS on silica is negligible, while the adsorption on alumina is high due to the different charge of the latter. Tests of adsorption of a modified polymer S-19703-35HT on alumina were also conducted at different pHs. Adsorption density decreases with pH. The results suggest that alkaline pH range is more cost-effective for a SDS/polymer system because of the low adsorption density.

A new term, reagent loss index (RLI), was used to analyze the adsorption data for different surfactants and minerals. It was shown that the chemical loss is very high in the case of SDS on

gypsum and limestone, while it is low in the case of silica. The mixed Dodecyl maltoside (DM)/C12SO3Na system was also evaluated using this standard term. It is fairly easy to find the optimal conditions, including mixing ratio and pH, for minimum chemical loss using polymer/surfactant mixtures.

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INTRODUCTION

Surfactant/polymer flooding is one of the promising techniques to recover residual oil from domestic oil reservoirs. However, the high cost of the processes as well as the significant loss of chemicals by adsorption on reservoir minerals and precipitations have limited the use of chemical-flooding operations. There is a need to develop cost-effective improved and innovative reagent schemes to increase recovery from domestic oil reservoirs efficiently. To achieve this goal, we have conducted systematic studies of adsorption of reagents on various reservoir minerals. Based on previous the results obtained, it can be inferred that interfacial behavior of surfactant mixtures can be manipulated by adjusting surfactant type and other parameters like mixing ratio and the order of addition. Currently, the aim of this project is to systematically analyze the data obtained to understand the mechanism of synergistic or antagonistic interactions between polymers and surfactants in bulk fluids and at mineral/fluid interfaces. In addition, we plan to develop a model to predict the performance of chemicals in enhanced oil recovery systems.

During the previous reporting period, we completed the wettability tests of alumina particles using two-phase extraction. The data were correlated to the adsorption results that have been previously reported. It was found that the wettability of the mineral surface is determined by both the nanostructure and the surface coverage. Water wettability (opposite to hydrophobicity) of alumina particles at pH 7 decreases with dodecyl maltoside up to the CMC, but increase again above the CMC because of formation of bilayers. Even though there is also a sharp increase of adsorption density due to the formation of hemimicelles at pH 4, the alumina surface remains hydrophilic at all of the surfactant concentrations tested due to low surfactant coverages – only about two percent of that at pH 7; Pyrene-probe fluorescence tests were also

done under the same conditions as that for wettability tests to elucidate the structure of microdomains formed at the solid/liquid interface. These results are in accordance with the wettability data.

During this period, we have also conducted adsorption tests of SDS and the modified polymer on both silica and alumina. It was found that SDS adsorbs strongly on alumina but very weakly on silica due to the different electrostatic forces. The adsorption density of both SDS and the modified polymer on alumina decreases markedly with pH, suggesting that alkaline range is more cost-effective with this surfactant/polymer system.

In addition, the term, Reagent Loss Index (RLI), proposed to evaluate the reagent loss of the desired chemical systems on different minerals. Using this framework involving RLI, it is easy to evaluate different systems and further it will be helpful in the selection of the most cost-effective reagents for oil recovery processes.

EXPERIMENTAL

MATERIALS

Surfactants

Several typical ionic and nonionic surfactants were selected for this study. During this period, anionic sodium dodecyl sulfonate ($C_{12}SO_3Na$) of ≥99.0 purity purchased from TCI Chemicals, Japan, Non-ionic sugar-based surfactant, n-alkyl-β-D-maltoside (>95% purity by TLC), from Calbiochem was also used as received.

Dodecyl Maltoside

Sodium Dodecyl Sulfonate

Figure 1 molecular structure of polymer used during this period.

Polymer

Modified polymer S-19703-35HT

Mineral Samples:

Solid substrate used during the current period is alumina AKP-50 obtained from Sumitomo. It has a mean diameter of 0.2 μm and the BET specific surface area of 10.8 m^2/g was measured using nitrogen/helium with a Quantasorb system. Its isoelectric point (iep) was determined to be 8.9. Silica obtained from Geltech has a mean diameter of 0.2 to 0.3 μm and has a specific surface area of 12.0 to 12.9 m^2/g and the isoelectric point of around 2.

Other Reagents:

HCl and NaOH, used for pH adjustment, are of A.C.S. grade certified (purity > 99.9%), from Fisher Scientific Co. To study the salt effect on surface tension, micellization and adsorption, salts NaCl, $CaCl_2$, $FeCl_2$, $AlCl_3$, Na_2SO_3, and $NaNO_3$ were obtained from Fisher

Scientific Co.; and sodium citrate from Amend Drug & Chemical Company, all of A.C.S. certified, and used as received. The water used in all the experiments was triple distilled and was tested for the absence of organics using surface tension measurements.

METHODS

Adsorption experiments

Adsorption experiments were conducted in capped 20 ml vials. Solid samples of 2 gram were mixed with 10 ml of triple distilled water for 2 hours at room temperature. The pH was adjusted as desired, and then 10 ml of the surfactant solution was added. The samples were equilibrated further for 16 hours with pH adjustment and then centrifuged for 30 mintues at 5000 rpm and the clear supernatant was pipetted out for analysis.

Wettability

The samples for determining relative hydrophobicity tests were prepared in the same way as the adsorption experiment, and the wettability was determined using liquid-liquid extraction technique. After 16 hours of equilibration, 20 ml of the slurry was transferred to a separatory funnel to which 15 ml of toluene was added. The mineral–surfactant–toluene dispersion was shaken for 1 minute manually and then allowed to settle for 1 hour. The bulk of the aqueous phase with hydrophilic solids, as well as the toluene phase with hydrophobic solids, was emptied out of the funnel separately. The two phases containing the solids were evaporated and the weight of the mineral was recorded. The hydrophobicity values were calculated using the equation:

$$Hydrophobicity = \frac{Weight\ \ of\ \ Particles\ \ in\ \ Toluene}{Total\ \ Particle\ \ Weight} \qquad (1)$$

Surface tension

The surface tension was measured at 25±1˚C using the Wilhelmy plate technique with a sandblasted platinum plate as the sensor coupled to a Cahn microbalance. The entire assembly was kept in a draft-free plastic cage at a temperature of 25 ± 0.05 ^{0}C. For each measurement, the sensor was in contact with the solution for 30 minutes to allow equilibration.

Analytical Techniques

The residual concentration of the anionic surfactant after adsorption was determined by a two-phase titration method using a cationic surfactant, dodecyl trimethyl ammonium chloride (DTAC), as the titrating solution. Concentration of the sugar-based surfactant after adsorption was determined by colorimetric method through phenol-sulfuric acid reaction. In ionic/nonionic surfactant mixtures, the total residual surfactant concentration after adsorption was obtained by adding the concentrations of the individual component surfactants, which were measured by either the two-phase titration or the colorimetric method.

Fluorescence Experiments

Sample preparation. For fluorescence measurements in solutions, the surfactant solutions were mixed with the desired amounts of pyrene probe, to make the final pyrene concentration ~ 1.0 μM. Surfactant solutions containing pyrene were shaken overnight at room temperature before fluorescence measurement. For fluorescence measurements at solid/solution interfaces, the same adsorption procedure was followed as in the experiments conducted in the absence of the probe. Desired amount of pyrene probe from stock solutions containing known amounts of pyrene was added into adsorption sample solution, to make the pyrene concentration ~ 0.2 μM. After separating the supernatant and the solid slurry by centrifugation, the solid slurry was taken for direct fluorescence measurements.

Steady-state experiments. Steady-state emission spectra were obtained using a Horiba Jobin Yvon Fluorolog FL-1039 spectrophotometer. A portion of the solid slurry sample from adsorption experiments or surfactant solution sample containing pyrene was transferred to quartz cells, and the samples were excited at 335 nm and their emission between 360 and 500 nm was recorded.

RESULTS AND DISCUSSIONS

1) Wettability of alumina due to the adsorption of surfactant mixtures

Adsorption of surfactants on solids could dramatically change the wettability of the surface. Wettability of alumina particles due to the adsorption of dodecyl sulfonate and DM mixtures has been investigated using two-phase extraction and deplection technique. The information on changes in wettability of the surface due to surfactant adsorption can also shed light on the orientation of the surfactant species on the solid surface and help to elucidate the relationship between molecular packing and structures.

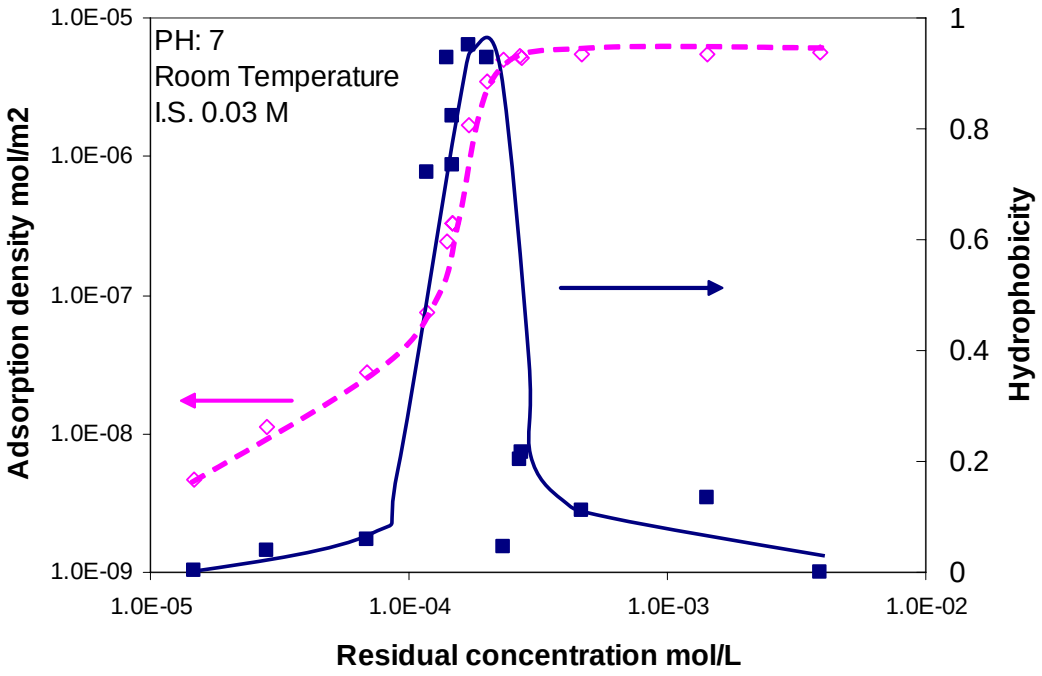


Figure 2. hydrophobicity of alumina along with adsorption at pH 7.

The effect of DM adsorption on the hydrophobicity of alumina is illustrated in figure 2 along with the adsorption isotherm at pH 7. Alumina becomes hydrophobic with the adsorption of DM and reaches maximum hydrophobicity around the CMC. Interestingly, the alumina remains hydrophobic only within a very narrow range and becomes hydrophilic again at higher surfactant concentrations. The drop in hydrophobicity suggests that additional surfactant molecules with hydrophilic groups orient towards the aqueous phase at higher concentrations. Evidently, in the low concentration range, a monolayer is formed with the surfactants adsorbed with the hydrocarbon tails oriented towards bulk and at higher concentration a bilayer with orientation of the hydrophilic head towards the bulk.

Hydrophobicity obtained in the case of mixed $C_{12}SO_3Na$/DM is shown in figure 3. In this case, the alumina surface exhibits hydrophobicity even in the low residual surfactant concentration range (below CMC), because of the strong adsorption of dodecyl sulfonate due to the electrostatic attraction. When the residual concentration reaches CMC, the alumina surface becomes hydrophilic again due to the formation of a bilayer.

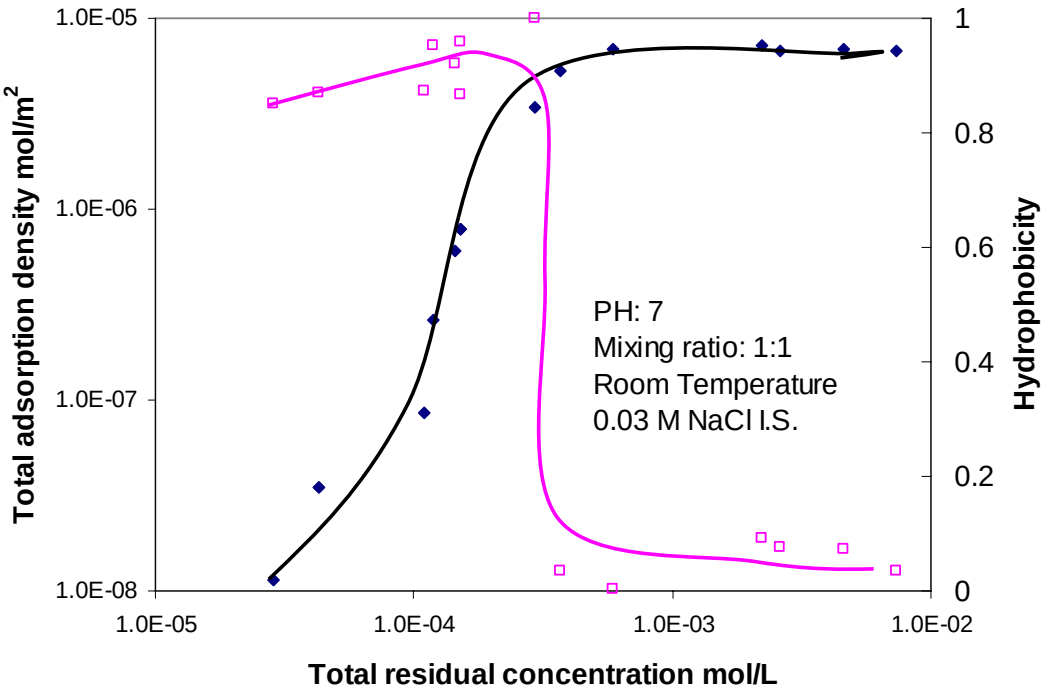


Figure 3. Effect of DM/sulfonate mixture adsorption on the hydrophobicity of alumina.

The effect of relevant parameters such as pH was studied next. It can be seen that pH has a marked effect on the adsorption of mixed $C_{12}SO_3Na$/DM on alumina. DM adsorbs fifty times less on alumina at pH 4 than at pH7, even though the adsorption isotherms have the same typical three-stage S shape (figure 4). The sharp increase at CMC indicates the formation of hemimicelles at the solid/liquid interface; however, the surfactant layer does not change the hydrophobicity of the surface due to the low surface coverage. The surface remains hydrophilic in the tested concentration range as shown in figure 4.

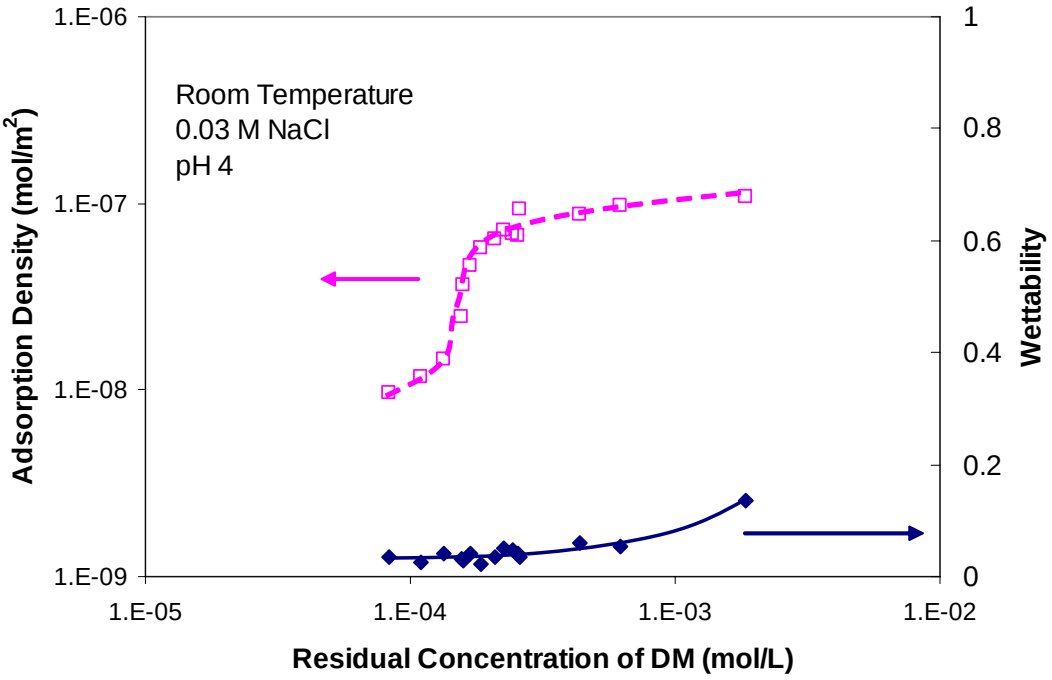


Figure 4. Effects of DM adsorption on hydrophobicity of alumina at pH 4.

2). Steady state fluorescence study of adsorption of Dodecyl Maltoside at solid/liquid interface.

Steady-state emission spectra were obtained using a Horiba Jobin Yvon Fluorolog FL-1039 spectrophotometer. A portion of the solid slurry sample from adsorption experiments or surfactant solution sample containing pyrene was transferred to quartz cells, and then the samples were excited at 335 nm and their emission between 360 and 500 nm was recorded. For fluorescence measurements at solid/solution interfaces, the same adsorption procedure was followed as for the experiments conducted in the absence of probe. After the adsorption reached

equilibration, the solid was separated from residual solution; and both the residual solution and the solid slurry were measured using fluorescence spectroscope.

The emission intensity from the residual solution and solids was plotted as a function of residual concentration in figure 5. The fluorescence intensity from the residual solution decreased sharply with concentration and becomes undetectable at CMC, as most pyrene molecules were extracted into the hemimicelles at solid/liquid interface. Interestingly, the intensity from the solids showed a sharp increase up to CMC and then decreased by almost half. The shape of the peak corresponded with the peak of hydrophobicity as shown in figure 6.

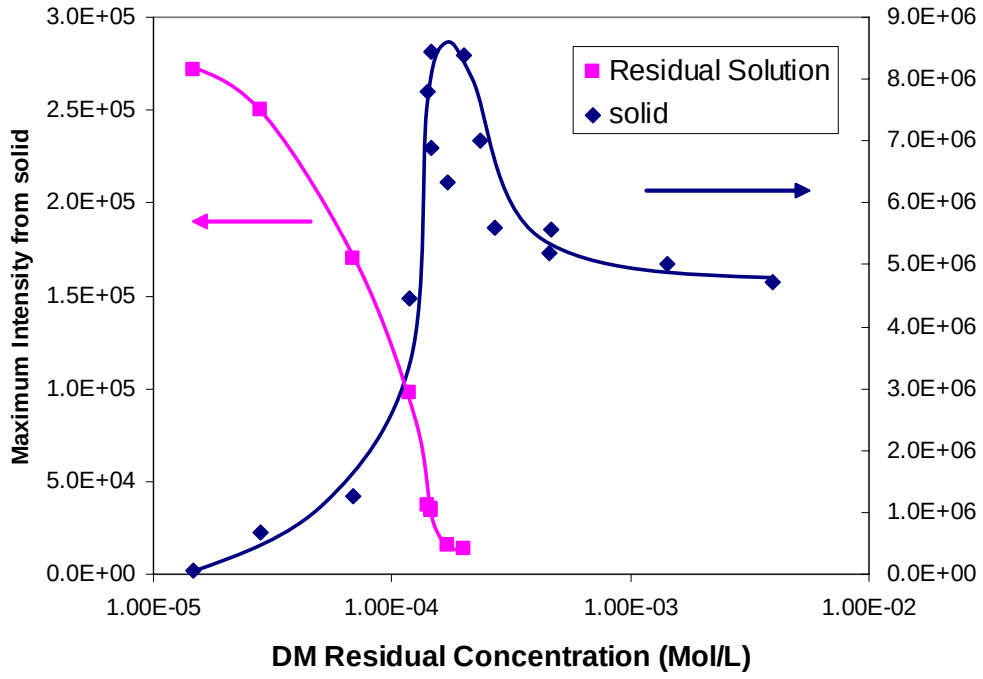


Figure 5. Effects of adsorption density on the intensity of pyrene emissions from solid and residual solution

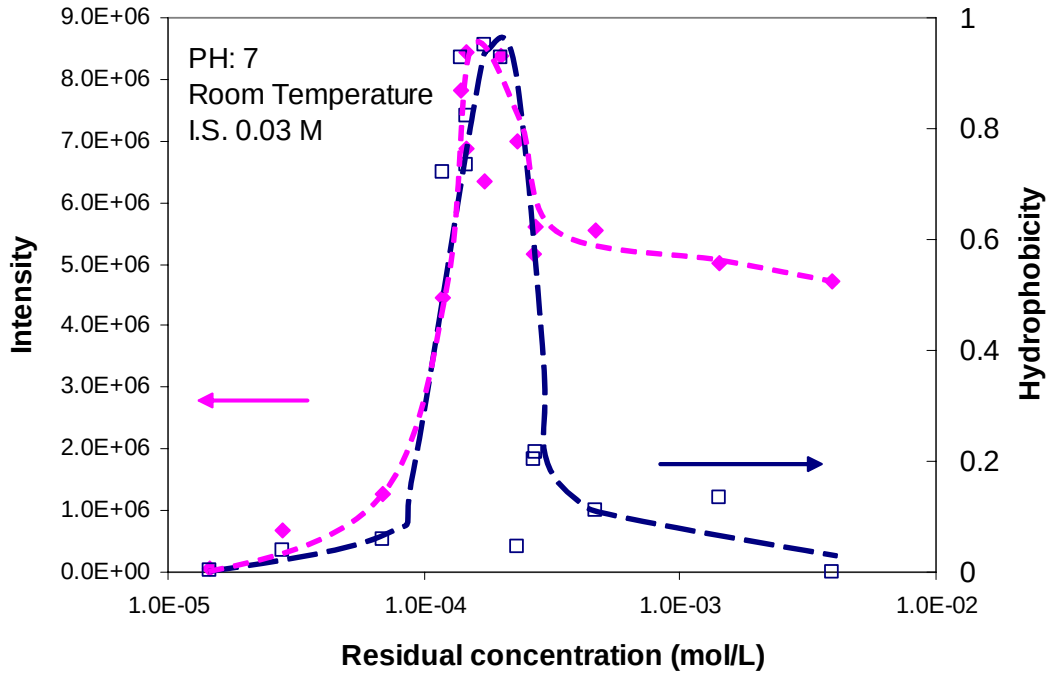
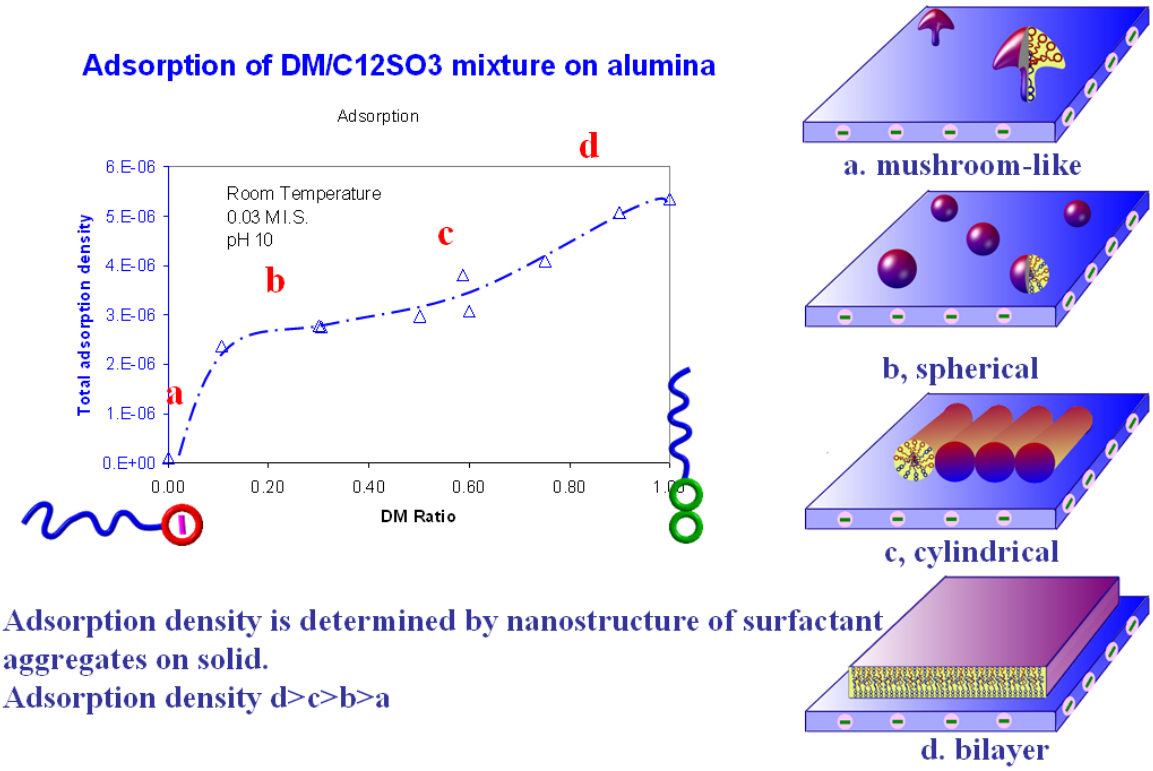


Figure6. Intensity of pyrene emission compared with hydropobicity of alumina surface at same adsorption situation .

3) nanostructure of mixed surfactants on minerals

Previous work has been done on interactions between surfactants and minerals in terms of adsorption of surfactants and wettability of minerals. It was found that the wettability of minerals particles is determined in terms of not only by the adsorption density but also the orientation of the surfactant molecules in aggregation. An example is given in figure 7. Adsorption tests were conducted with mixtures of sodium dodecyl sulfonate and sugar-based n-dodecyl-β-D-maltoside (DM) on alumina minerals at different surfactant mixing ratios. The total adsorption density is less than 50% of that at other pH levels below a mixing ratio of 0.6, but the mineral surface is surprisingly hydrophilic under this condition, which suggests that the head groups of surfactant

molecules are orienting towards the bulk solution. This condition is beneficial for efficient chemical flooding.



Adsorption density d>c>b>a

Figure 7: Molecular packing at solid/liquid interface determines the loss of reagents in improved oil recovery

Possible nanostructures formed in different mixing ratio range were speculated and illustrated on the right of figure 7, which shows that the nanostructure is determined mainly by the mixing ratio. In b and c ranges, the mineral surface is hydrophilic, even though the surface is not fully covered, because of the spherical and cylindrical structures, in which, the surfactant molecules arranged on the top have the head groups oriented towards water.

4).Adsorption of SDS and modified polymer on alumina

Adsorption of SDS on alumina was tested at both pH 4 and pH 7. The adsorption isotherms are shown in figure 8. At pH 4, SDS reaches plateau adsorption range at lower concentrations due to the strong electrostatic attraction between negatively charged surfactant molecules and the positively charged mineral surface. At pH 7, the adsorption reaches plateau at concentrations close to the CMC of SDS because of the neutralization of the positive charges on alumina surface.

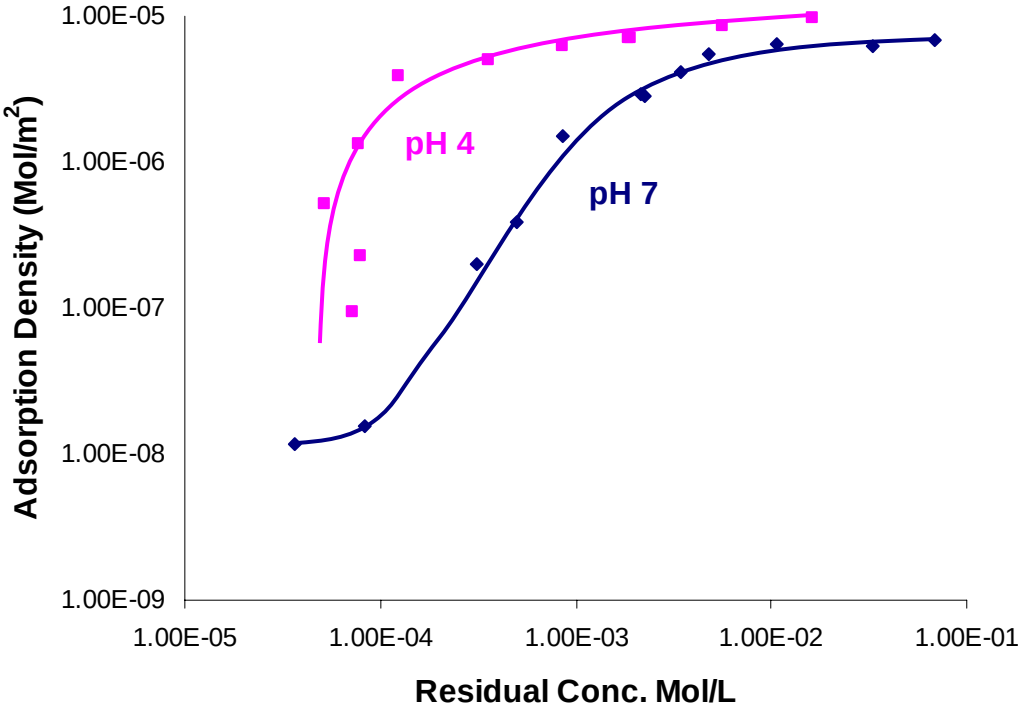


Figure 8 Adsorption of SDS on alumina at pH 4 and pH 7

Tests have been conducted to investigate the adsorption of the modified polymer on alumina at pH 4, 7 and 10. The results are shown in figure 9. It was found that pH plays an important role in the adsorption of the polymer on alumina. The adsorption density at pH 10 is smaller than 50% of that at pH 4, suggesting the electrostatic force to be one of the driving forces.

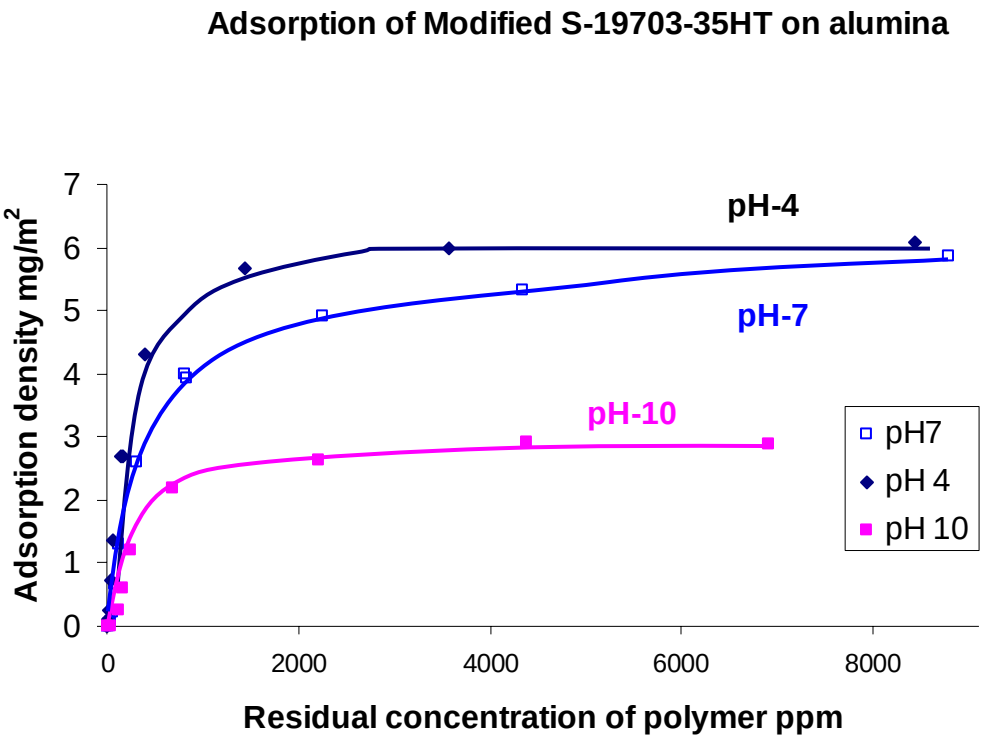


Figure 9 Adsorption of modified polymer on alumina at different pHs

5). Modeling of surfactant adsorption on solid surfaces.

A new term, "Reagent Loss Index (RLI)", was proposed previously to evaluate the performance of a surfactant in a standardized framework in order to evaluate the adsorption behavior of different surfactants on varied minerals and then take the molecular structure into account to develop a structure performance relationship eventually. The RLI is defined as the ratio of the actual loss due to adsorption and precipitation to the theoretical maximum adsorption, Ads_0, when a complete double layer is formed at solid surface.

Some of the previous adsorption results were categorized into 6 Reagent Loss Index (RLI) range as shown in table 1.

Table1. Typical ranges of Reagent Loss Index and examples.

Reagent Loss Index (RLI) range	**Phenomena**	**Cases**
0	**No adsorption**	Ionic surfactant alone on solid surfaces with same charge
~0	**Negligible adsorption**	Dodecyl maltoside on silica
0~0.5	**Medium adsorption**	DM on alumina in pH range 3~6
0.5~1	**Strong adsorption**	DM on alumina in pH range 7~10
1~	**Enhanced adsorption**	Ionic surfactant on highly oppositely charged mineral surfaces
>>1	**Precipitation**	Sodium Dodecyl Sulfate on gypsum and limstone.

Adsorption data of SDS on four different minerals: alumina, silica, gypsum and limestone, have been analyzed and the reagent loss indexes obtained are listed in table 2. The high chemical loss in the cases of gypsum and limestone is due to precipitation caused by the possible calcium ions. From the table, it can be concluded that SDS could be used in those containing alumina and silica but should be avoided for used in oil reservoirs containing gypsum or limestone.

Table 2 Reagent Loss Index for SDS on different minerals

Minerals	Surfactants	pH	Adsorption	**Reagent Loss Index (RLI)**
Alumina	SDS	pH 4	1.04E-05	1.8
Alumina	SDS	pH 7	6.95E-06	1.2
Silica	SDS	pH 7	1.24E-07	0.02
Gypsum	SDS	pH7	0.00037	64.9
Limestone	SDS	pH 7	5.07E-05	8.8

Table3. Reagent Loss Index for DM/ C12SO3Na mixture on alumina

Surfactants	pH	Mixing Ratio	Adsorption	**Reagent Loss Index (RLI)**
DM	pH 7	1:0	5.63E-06	0.78
DM	pH 7	3:1	5.11E-06	0.71
DM	pH 7	1:1	2.19E-06	0.30
DM	pH 7	1:3	1.5E-06	0.21
C12SO3Na	pH 7	3:1	2.21E-06	0.39
C12SO4Na	pH 7	1:1	3.92E-06	0.69
C12SO5Na	pH 7	1:3	5.45E-06	0.96
DM	pH 4	1:1	2.72E-06	0.38
C12SO3Na	pH 4	1:1	5.81E-06	1.02
DM	pH 10	1:1	1.95E-06	0.27
C12SO3Na	pH 10	1:1	2.37E-06	0.42

Moreover, the analyzed adsorption data of mixed DM/C12SO3Na and the reagent loss index at different mixing ratio and pH are listed in table 3. It was observed that at pH 10 both

DM and C12SO3Na have the lowest adsorption, suggesting that alkaline pH range is the most cost-effective for this mixed systems for oil recovery.

SUMMARY AND CONCLUSIONS

The wettability changes of alumina with surfactants adsorbing on the surface and the adsorption of modified polymer were investigated during this period to elucidate mechanisms of interactions of molecular structures from a fundamental point of view. The wettability of alumina was found to be determined by both the nano structure of the hemimicelles and the surface coverage.

Polarity results measured by fluorescence are in good agreement with the wettability results. The fluorescence intensity changes in the residual solution and at the solid surface indicated formation of hemimicelles on solids. At pH 7, a narrow hydrophobic range was found with DM for alumina by both wettability and fluorescence tests.

A new term, reagent loss index (RLI), was used to evaluate different surfactants and their mixtures on various mineral surfaces. This term can be used for designing and screening of chemical formula in oil recovery. Since the RLI is a standardized term, the adsorption behavior of surfactants in different cases can be compared.

Publications and Presentations

1) Shaohua Lu and P. Somasundaran, Analytical ultracentrifuge study of micellization of surfactant mixtures, Oral Presentation The 231st ACS National Meeting, Atlanta, GA, March 26-30, 2006

2) Shaohua Lu and P. Somasundaran, Synergy Among Surfactants in Solution and on Particles in Suspensions. Industrial Advisory Board meeting in University of Florida, Feb 21 2006, (Received Best Poster Reward).

3) Shaohua Lu and P. Somasundaran, Rock Wettability Control and Chemical Loss Reduction, 2006 AAPG Rocky Mountain Section Annual Meeting (June 11-13, 2006).

4) Shaohua Lu and P. Somasundaran, Solution behavior of nonionic/anionic surfactant mixtures, The 16th International Symposium on Surfactants in Solution KOREA, June 2006.

5) Shaohua Lu and P. Somasundaran, Synergy among Surfactants in Solutions and on Particles in Suspensions. 12^{th} IACIS.

FUTURE PLANS

For task 2:

- The effects of dissolved species (multivalent and univalent ions, such as Na^{+}, Mg^{2+}, Fe^{2+}, SO_4^{2-} etc) on the adsorption of selected surfactant / polymer systems on minerals under various conditions will be studied. The effect of polymers on the adsorption of surfactant on various types of miners such as alumina will also be further investigated. Adsorption, abstraction and precipitation studies will be conducted to find out optimum formulation to minimize the loss of chemicals due to precipitation.

For task 3:

- Selection of optimal formulations under simulated reservoir conditions: selected experiments will be conducted in the lab under representative reservoir conditions (pH, salinity and temperature) to establish the validity of the optimal processes. Phase diagram of mixtures of representative oil and optimal formulations, possibly mixtures of surfactants and polymers, will be examined to determine the possibility of formation of emulsions in the presence of dissolved multivalent ions from minerals.

For task 4:

- Previously reported data will be analyzed using the standardized framework and then models will be developed to obtain a better quantitatively understanding of the interaction between minerals and surfactants/polymers, the precipitation of chemical reagents due to the dissolution of multivalent ions from the minerals, and the performance of the formulations under reservoir conditions. Based on the models, a guidebook containing

optimally desirable chemical combinations will be organized to facilitate the evaluation of formulations of the surfactant/polymers for different reservoir mineral environments in terms of several key parameters.